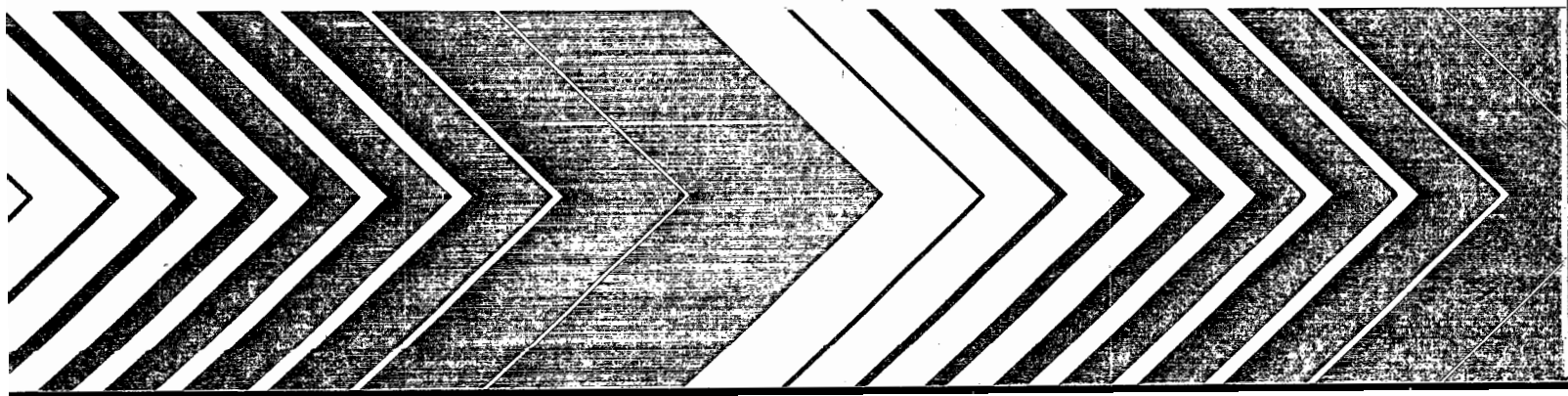


Research and Development



# Removal and Recovery of Metals and Phosphates from Municipal Sewage Sludge



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REMOVAL AND RECOVERY OF METALS AND PHOSPHATES  
FROM MUNICIPAL SEWAGE SLUDGE

by

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## FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report presents the results of a study that looked at the technical and economical feasibility of removing and then recovering the heavy metals and phosphates present in phosphorus-laden chemical sludge. The results should be valuable in considering future research effort in this area.

Francis T. Mayo, Director  
Municipal Environmental Research  
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## ABSTRACT

This research program was undertaken to yield more extensive laboratory data for the acid extraction process described by Scott and Horlings in 1975, which was found to be a simple method of extracting metals and phosphate from chemical type municipal sludges. The data were desired for different types of sludges in order to assess the benefits of this process and to estimate probable costs at different conditions.

Two sludges were used, an anaerobically digested chemical sludge to which ferric chloride had been added as a phosphate precipitant; and an aerobic waste activated sludge to which alum had been added for phosphate control. Both sludges were dewatered and incinerated in multiple hearth incinerators at their respective plants, the aerobic sludge, however, being first combined with settled primary sludge. Hence filter cake samples were also used as starting materials.

Adequate extractions (about 80% or more) of phosphorus, iron, aluminum, zinc, magnesium, nickel and manganese can be obtained from either sludge or filter cake at a pH of 1.5, using sulfuric acid. Chromium extractions are less predictable, and vary from 50%-90%. Copper cannot be extracted from anaerobic sludge, but does extract from aerobic systems. Lead, which forms an insoluble sulfate, is not extracted. Iron is in the ferrous form in anaerobic systems but in the ferric form in aerobic systems.

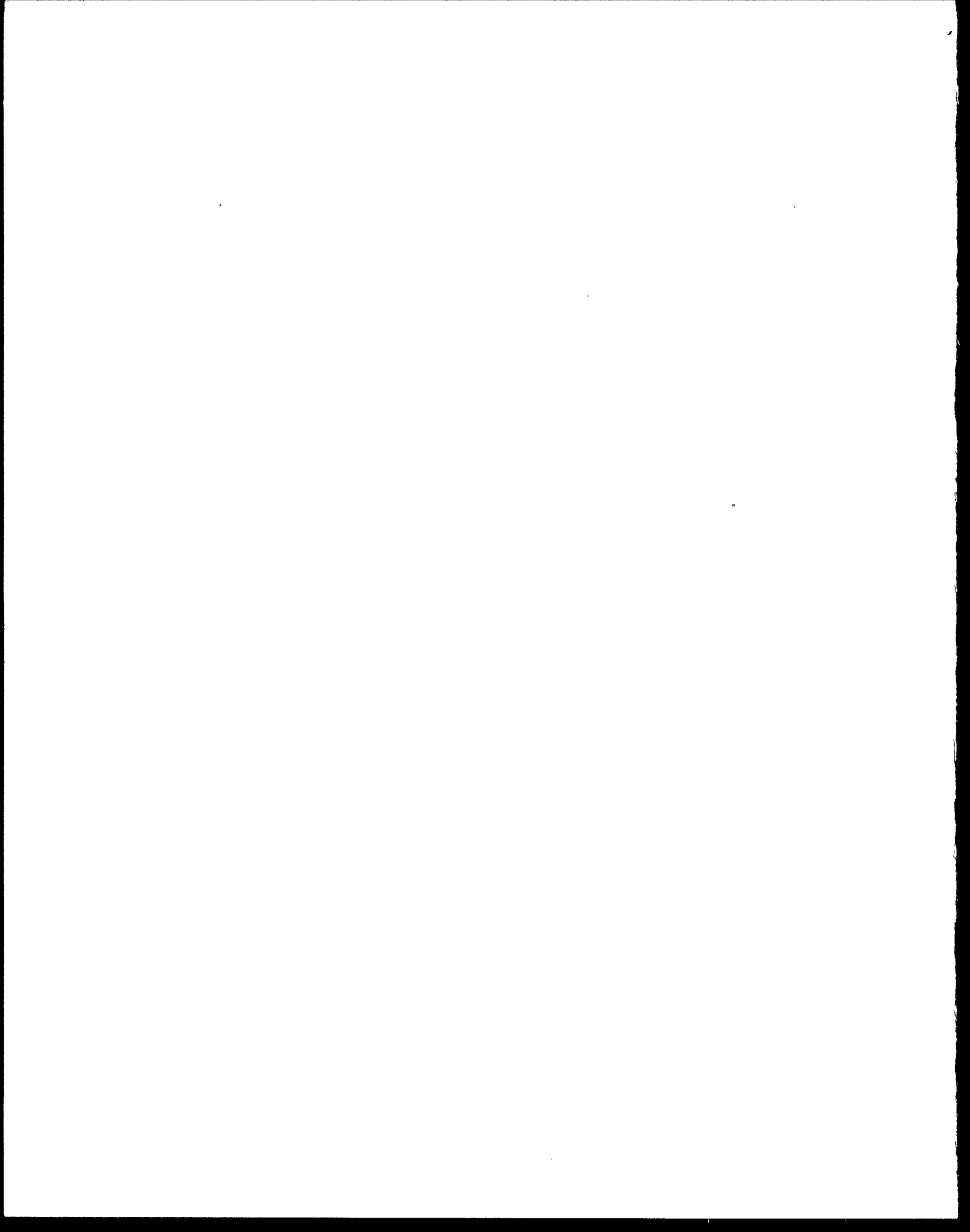
The resulting acid extracted residual solids show a removal of from 50%-70% of the ash-forming inorganics. The calorific value increases from 30%-40%, because only from 7%-10% of the organic matter or COD is extracted by the acid.

Acid extraction by the method proposed here (20 minutes extraction followed by five minutes of heating) appears to improve filterability of anaerobic sludges somewhat, but has no significant effect on aerobic sludge.

The acidic extract solution can be separated into fractions by selective precipitation using lime as a neutralizing agent. Extracts containing ferrous iron can be separated into a solid containing most of the Al, Mg, Cr and P and a liquid containing most of the iron by precipitation at pH 4.5. The liquor can be recycled back to the plant for phosphate removal. Extracts rich in aluminum or ferric ion can be separated into a solid containing essentially all the Fe, Mg, Al, Ni, Mn and P by precipitation at pH 4.0. This solid can then be further separated by successive treatment with ammonia and sodium hydroxide.

Costs of the process were estimated for each of the two plants from which samples were obtained. The larger plant (180 mgpd) producing an iron rich anaerobic sludge gave a cost of \$33 per million gallons of influent, after credits for iron and phosphate were taken, but without credit for savings in incineration costs or ash disposal. The smaller plant (30 mgpd) gave a cost of \$50.70 per million gallons of influent on the same basis. Some of this higher cost for the smaller plant results from the more extensive treatment required for chemical recovery. The major cost factor in the total process is the cost of reagents, with this being about 60% of the total cost.

This report was submitted in fulfillment of EPA Grant R-804669 by Donald S. Scott under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1, 1976 to December 31, 1978 and work was completed as of October 1, 1978.





## CONTENTS

Foreword . . . . .	iii
Abstract . . . . .	iv
Figures. . . . .	viii
Tables . . . . .	ix
Acknowledgement. . . . .	x
1. Introduction . . . . .	1
2. Conclusions. . . . .	4
3. Recommendations. . . . .	5
4. Materials. . . . .	6
5. Experimental Procedures. . . . .	8
6. Results and Discussion . . . . .	11
7. Estimates of Cost. . . . .	28
References . . . . .	33

FIGURES

<u>Number</u>		<u>Page</u>
1.	Amount of metals precipitated vs pH . . . . .	20
2.	Residual fraction of metals in the extract as a function of pH . . . . .	21
3.	Acid requirement of sludge to attain a given pH value . . . .	22

## TABLES

<u>Number</u>		<u>Page</u>
1.	Characteristics of sludge samples . . . . .	11
2.	Analysis of original samples. . . . .	12
3.	Extraction conditions . . . . .	13
4.	Analysis of extract solutions . . . . .	13
5.	Solids content of filtered extracts . . . . .	14
6.	Extraction results. . . . .	15
7.	TOC and COD analysis. . . . .	16
8.	Filtration tests. . . . .	17
9.	Precipitation test at pH 4.5. . . . .	18
10.	Extraction conditions . . . . .	19
11.	Percent extraction of metallic elements . . . . .	23
12.	Solids content of filtered extracts . . . . .	24
13.	Extraction residues . . . . .	25
14.	COD analysis. . . . .	25
15.	Ash fusion points . . . . .	27

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The cooperation is gratefully acknowledged of the staff of the Ash-bridge's Bay wastewater treatment plant of the Metropolitan District of Toronto, and of the staff of the wastewater treatment plant of the city of Warren, Michigan, both of whom supplied samples and plant operating data.

Most of the laboratory tests and analyses were done by, or under the direction of, Mr. Harry Horlings, Research Associate in the Department of Chemical Engineering, University of Waterloo. His skill and enthusiasm were essential for the completion of this work.

## SECTION 1

### INTRODUCTION

Sewage sludge is one of the end-products of the physical, chemical and biological operations employed in modern municipal wastewater treatment systems. Effective sludge management and disposal is a problem and a challenge in treatment plants, particularly those of large capacity located in highly urbanized areas. The upgrading of treatment plants, particularly the addition of phosphorus removal practices, results in increased volumes of biological or chemical sludges, which may be more difficult to handle than a simple primary sludge. As treatment plants become more sophisticated, the sludge handling and disposal problem grows.

There is at present no means of disposing of final sewage sludge at a profit, and so sludge remains a growing liability for the plant operator. In fact it has been estimated that treatment and disposal of sludges produced in municipal wastewater treatment plants can account for up to 60% of the total cost of operating these facilities (1). A number of methods of sludge disposal exist which are presently viable for urban plants such as agricultural land disposal, land reclamation, sanitary land filling and incineration. Recently, however, there has been a growing concern that the heavy metals content of either sludge or incinerator ash is not adequately fixed, and can re-enter the ecology by leaching and/or plant uptake. Relatively little is known concerning the uptake of heavy metals by plants from contaminated soils, and it is only recently that systematic research into this potential problem has been undertaken, for example (2-8). Preliminary results show that certain combinations of the right type of plant, soil and metallic element can lead to undesirable metal concentrations in plant foods, or to deleterious effects on plant growth. In Canada, limits to the use of sludge for application to agricultural land are now being considered, and such limits already exist in England.

Land for disposal of sewage sludge as sanitary land fill, drying beds, or lagoons is becoming increasingly difficult to find and increasingly costly in the vicinity of large urban centres. In addition, the sludge volume increases annually, and as more chemical sludges are produced with higher metal and phosphate contents, suitable land disposal will become more and more costly and difficult.

Because of these considerations, incineration is growing in popularity as a final disposal process for sludge. In fact, incineration is a final disposal mechanism only for the organic part of the sludge, and the inorganic constituents are left as an ash, high in metals and phosphorus content. Recently, studies have been carried out and are currently underway to attempt

to assess the nature of this ash and to explore ways of recovering metals or phosphate from it (9-13). Presently available results suggest that the ash is sufficiently refractory that extraction of metals and phosphate from it is difficult in any reasonable yield or at reasonable cost. Ash quantities are considerably increased in chemical sludges due to the added metal salts and the precipitation of phosphates. One study has shown that neutral water can leach some metals, e.g., chromium, out of the ash in sufficient quantities to cause groundwater contamination (9).

Despite possible problems with the quantity and nature of the ash, incineration is the most rapidly growing method of sludge disposal (at present over 200 installations in the United States). If it were possible to remove metals and phosphate from sludge prior to incineration, the resulting ash would be innocuous with a low metal content, the ash volumes would be reduced, and the calorific value of the sludge feed to the incinerator would be enhanced. If the metals and phosphates could be recovered in usable form, their value might help to offset the cost of removal. An anaerobically digested sludge might profit the most from such treatment, as the metals and phosphates (and ash content) are highest in these sludges because of the reduction in organic mass during digestion.

The present work was undertaken to extend the initial preliminary work of Scott and Horlings (14)(15) who found that brief extraction of the sludge at 20°C with acid in modest excess would successfully solubilize from 80%-100% of most cations as well as the phosphate ion. Further, a rough separation of the metals could be made by selective precipitation.

A follow-up study was carried out by Oliver and Carey (10) who examined a number of sludges for their acid extractability using a titration technique with sulfuric acid. They found that little metal extraction occurred after reaching a pH of 1.5, and that extractability of a given metal varied widely depending on the nature of the sludge. In general, they report somewhat lower extraction yields than do Scott and Horlings for similar sludges. Most of the sludges tested by Oliver and Carey had been anaerobically digested, but only five were chemical sludges. In this latter group, generally 70%-100% of the nickel, cadmium, iron, aluminum and phosphorus could be extracted at a pH of 1.5 under their conditions. Copper and lead did not extract from anaerobic sludges, and the behavior of chromium and zinc was unpredictable, although generally better than 50% up to 90% extraction occurred. The failure of copper to extract was assumed by Oliver and Carey to be due to organic complexing, whereas Scott and Horlings assumed the copper to be in a univalent state. Oliver and Carey also attempted to extract sludges with ammonia and ammonium salt mixtures, but found that soluble metal yields were low.

Electrochemical plating of zinc, copper, cadmium and nickel was also attempted from sludge and from clear acid extract solutions by Oliver and Carey. The latter worked well, but attempts to plate from sludge did not give useful yields. Cost estimates for the extraction and recovery process were done only for reagent costs, and processing costs were not worked out. They concluded that incinerator ash might be

a better starting material than sludge but did not evaluate the economics here either, except to conclude that they did not appear to be favorable. On the other hand, the study done by Cambrian Process Ltd. (9) concludes that the major metals, iron and aluminum, as well as most of the minor ones such as zinc and chromium are so refractory in incinerator ash that a useful degree of metal recovery can only be achieved by treatment before incineration.

The economic estimates made by Oliver and Carey are not adequate to allow any decision to be made concerning the costs of either the acid leaching of sludge or the treatment of incinerator ash. Additional studies are now underway, or have been recently reported, concerning methods of recovery of metals or phosphate from incinerator ash, and better economic estimates may soon be available.

The objectives of the present study were to carry out evaluations of the acid extraction process, as originally described by Scott and Horlings, for chemical sludge from a plant employing anaerobic digestion, and for a second sludge from a plant using aerobic (activated) sludge processes. In particular, the effect of the acid extraction process on the quality of the sludge as an incinerator feed was of interest. Data were also desired which would allow a cost estimate to be made of the cost of acid extraction treatment, and an estimate of the possible value of recovered chemicals.

Advantages of acid extraction of sludge prior to incineration result from the reduction in ash mass and volume, the increased calorific value and the absence of large amounts of metals in the ash. If the sludge is not incinerated but is used for agricultural purposes, acid extraction would yield a sludge from which most of the nickel, cadmium, chromium and zinc (all known to be injurious to crops) had been removed. Although the phosphorous content of the sludge would be reduced, the resulting extracted residual solids would in fact probably show a better nitrogen to phosphorus ratio than the original sludge, which is relatively too rich in phosphate.

## SECTION 2

### CONCLUSIONS

This work has demonstrated the technical feasibility of the acid extraction process for municipal chemical sludges of widely varying types. Depending on the nature of the sludge, it is equally feasible to recover chemicals or metals from the extract solutions.

However, the cost of the extraction and recovery process is such that the value of recovered chemicals or metals will only pay 20%-30% of estimated annual total cost. The major cost factor is the expense of reagents for recovery of chemicals, and cost reduction would be most readily achieved by developing better methods for treating extract solutions.

For large plants the cost of removing metals and phosphates might be warranted if fuel costs are high for incineration, or if ash disposal is a major problem. In the present stage of development, the process does not appear to be likely to show benefits commensurate with costs for medium size or small treatment plants.



### SECTION 3

#### RECOMMENDATIONS

If a larger scale treatment plant can be identified which is having problems with high costs for incineration, or difficulty in disposing of ash, it would be worthwhile to assess the behavior of the sludge filter cake feed to the incinerator in the acid extraction process. The process is most likely to work well for anaerobically digested sludge, although it performs well on a wide variety of sludge.

Some further experimentation might be warranted in assessing filterability characteristics and means of improving these for acid treated sludges, especially for aerobic sludge or primary sludge. Further work to reduce the cost of separating iron or aluminum, and phosphate, from the extract solutions might make the process nearly self-financing for larger plants.

## SECTION 4

### MATERIALS

As the present project deals with the evaluation of an acid extraction process for chemical sludges from municipal waste water treatment plants (i.e., those sludges produced in plants in which a chemical precipitant has been added, primarily for the removal of phosphate) typical materials were sought for the initial evaluation. The anaerobically-digested sludge produced by the main treatment plant of the Metropolitan District of Toronto, Canada at Ashbridge's Bay, Toronto, was one chosen for this purpose. A second choice was the aerobic sludge, and mixed sludge incinerator feed, produced by the municipal treatment plant of Warren, Michigan.

The Ashbridge's Bay plant is currently 180 million gallons/day treatment capacity and is presently undergoing a substantial expansion. It incorporates in the existing plant secondary activated sludge treatment, which since December, 1976, has also included addition of ferric chloride as a phosphate precipitant. Waste activated sludge is anaerobically digested, the underflow from these digesters is treated with polymeric flocculants and then de-watered. The de-watered sludge cake is incinerated in large multiple hearth furnaces.

On February 15th, 1977, samples were obtained from the Ashbridge's Bay plant of the thickened underflow from the anaerobic digesters (Sludge A) and of the de-watered sludge cake (Cake A) being fed to the incinerators. The primary material for evaluation was the thickened underflow from the anaerobic digesters, since the acid extraction process proposed in this project for chemical sludges may alter their filtering characteristics as well as the chemical composition, and hence the de-watered sludge presently produced might not be a preferred starting material for acid extraction. On the other hand, the sludge filter cake can be re-slurried to 10%-11% solids, and acid extraction of this slurry yields a much richer extract and minimizes process equipment volume.

It is interesting to note that the Ashbridge's Bay expansion will include heat treating units using both the Porteous and the Zimpro methods, and hence yet a third potential starting material for acid extraction studies may soon be available.

All samples were stored at 0° - 1°C throughout the test period.

The sludge filter cake differs in composition from the digester underflow only in moisture content and by the addition of small amounts of a polymeric conditioner prior to de-watering.

The second set of samples was obtained from the municipal wastewater treatment plant of Warren, Michigan, a northern suburb of Detroit. This plant is operated as two 18 mgpd plants, for a total capacity of 36 mgpd. The plant serves a population of 180,000, and the area is the home of a number of industries (General Motors Technical Center, Detroit Tank Arsenal, and factories producing steel, electrical equipment and tools and dies). The waste water treatment facility consists of mechanical screening, grit removal, primary settling yielding a primary sludge, aeration, final settling, sand bed filtration and chlorination. Phosphate reduction is accomplished by alum addition prior to final settling at an average dosage of 71 ppm. Waste activated sludge is concentrated to about 4% solids, together with backwashings from the sand filters used for effluent final polishing, in a Komline-Sanderson pressure flotation unit. Samples of this thickened sludge were one of the primary materials studied in this work (Sludge B). The waste activated sludge solids from the flotation step are mixed with primary sludge, a cationic flocculant is added and the mixed sludge is dewatered by vacuum filtration, and then incinerated in a standard multiple hearth incinerator. Samples of the incinerator feed filter cake (Cake B) were the second material used for acid extraction tests. In addition, samples of incinerator ash were taken.

Sampling was done at 12:00 noon on December 13, 1977. All samples were returned immediately to the laboratory and stored at 2°C. Experience has shown that chemical behaviour is unchanged at this temperature. However, the sludge ages rapidly with respect to the flocs formed by the polymeric coagulants, and so filtering behaviour deteriorates rapidly to that of an untreated (by polymeric filter aids) sludge.

In this plant, it is likely that the mixed sludge feed to the filters, or the filter cake would be a suitable raw material for an acid extraction step.

Thickened sludges and filter cakes were sampled by taking lots of several gallons from process streams. In a micro sense, these materials were not particularly homogeneous, and great care was found to be necessary in taking small samples for laboratory analysis from these larger samples. Intense agitation before sampling and duplicate analyses on different samples were found to be necessary to obtain consistent results. (repeated values with + 2%).

## SECTION 5

### EXPERIMENTAL PROCEDURES

#### Moisture Content and Elemental Analysis

For the basic characterization of the sludge, Method I proposed by Van Loon (16) was adopted. For moisture determinations, this requires drying of the sludge at 110°C for 16 hours. Digestion of the sludge was done using nitric acid - hydrochloric acid mixtures as recommended by Van Loon (16). All metallic elemental analyses were done by atomic absorption spectroscopy using a Perkin Elmer Model 303 spectrophotometer. For most determinations the nitrous oxide-acetylene flame was found to give better sensitivity than the acetylene-air flame.

Phosphorous was determined as orthophosphate using the method outlined by Murphy and Riley (17). In this procedure ammonium molybdate and potassium antimonyl tartrate are reacted in the presence of sulfuric acid with dilute solutions of orthophosphate to produce the phosphomolybdate ion  $PO_4 \cdot 12 MoO_3^{3-}$ . This complex ion is then reduced by the addition of ascorbic acid to produce the intensely colored "molybdenum blue" which reached maximum color intensity within ten minutes. The optical density of the samples was then read at a wave length of 882 m in a calibrated spectrophotometer. Details of reagents and procedures can be found in the original paper of Murphy and Riley.

#### Dissolved Solids, Volatile Solids and Ash Contents

Dissolved solids in extract solutions or in sludge were determined by evaporating a known volume to dryness at 103°C for a minimum time of nine hours.

Volatile solids were determined by firing a known weight of dry solids in a muffle furnace at 600°C for 20 minutes. The residue was allowed to air cool, and then desiccated and weighted.

Ash content was found by firing a known weight of dry dissolved solids or dried sludge solids in a muffle furnace at 800°C for two hours, cooling, desiccating and weighing.

#### Total Organic Carbon

These values were found in the usual way by the difference between total carbon values and inorganic carbon values.

Total carbon and inorganic carbon were measured using a Beckman Model 915 Total Organic Carbon Analyser. Total organic carbon was found by the difference between two successive identical samples, total carbon being measured for one and inorganic carbon for the other.

#### Chemical Oxygen Demand

The standard method of the Water Pollution Control Federation, 13th edition (18) was used for this determination.

#### Calorific Values

Calorific values of sludges, filter cakes or residues from extraction were determined in a standard Parr Oxygen Bomb Calorimeter.

#### Filterability

Filterability was measured by both the Buchner funnel filtration test as described in Manual 20 of the Water Pollution Control Federation, (19) and by the filter leaf test. The latter employed a Dorr-Oliver Test Leaf filter, 11 cm. diameter with a No. 114 fast filtering Whatman filter paper as filtering medium. The test was done with a vacuum of 15 inches of mercury, submergence time of one minute and a drying time of two minutes.

#### Ash Softening Point and Fusion Point

No standard procedure is available for the measurement of softening or fusion points of ash from sewage sludge. Therefore, the ASTM procedure outlined for ash from coal or coke was adopted (20), using cones in the shape of triangular pyramids 1/4" on the base and 3/4" high, prepared in a special brass mold according to the ASTM specification. Heating was done in a temperature-controlled muffle furnace with a mildly reducing atmosphere with a heating rate of between 5° - 10°C per minute.

#### Acid Extraction of Sludge

Sludge extraction was performed using sulfuric acid and procedures found by Scott and Horlings (2) to be nearly optimal. For the digester sludges, to 0.5 kg. of sludge "as-is", concentrated (97%) sulfuric acid was added at room temperature slowly until a desired final pH value had been reached (final pH values of either 1.5 or 0.8 were used as standard in these tests). Reaction was allowed to proceed for 20 minutes with stirring, and the extract mixture was then brought to a boil and boiled for five minutes. After cooling to 65°C, the mixture was vacuum filtered, the residue washed several times, and filtrate and washing combined diluted to 1000 ml. It was this resulting extract solution which was used for all analyses. In some tests with the aerobic sludge, for which adequate washing was difficult, the undiluted extract was analysed also.

Extraction of the de-watered sludge cake sample was similar except that 0.4 kg. of "as-is" cake were mixed before acidification with 385 mls. of water to give a slurry of suitable consistency. The filter cake contained

a polymeric conditioner which was not present in the digester underflow samples. It was found that about 11% solids was the maximum concentration for which slurry viscosity was still acceptable.

#### Precipitation of Metals from Extracts

To a portion of clear acid extract solution measured volumes of either standard sodium hydroxide solution or known weights of calcium hydroxide, were added slowly with agitation until a desired pH value was reached. Stirring was continued for a further 10 minutes while adjusting the pH until a reasonably constant value was obtained. The solution was then filtered and the filtrate analysed and the percentage precipitation of the metal calculated.

## SECTION 6

## RESULTS AND DISCUSSION

Characterization of Sludge Samples

The original sludge sample was characterized to give basic information by which to judge the effects of acid extraction. Results are shown in Table I.

TABLE I. CHARACTERISTICS OF SLUDGE SAMPLES

Property	Sludge A Digester Underflow	Cake A De-watered Sludge Cake	Sludge B Flotation Waste Act. Sludge	Cake B Mixed Sludge
% Dry Solids	3.16	14.51	4.09	13.4
% Ash	47.62	46.40	34.9	32.5
pH	7.9	7.6	6.7	6.7
% Volatile Solids	54	53	57.2	61.3

Elemental analysis was carried out on three of the above samples (Sludge A, Sludge B and Cake B) after digestion in an HCl-HNO<sub>3</sub> mixture, and the results are given in Table 2. Cake B was not analysed since it had essentially the same composition as Sludge A. The incinerator ash from the Warren, Mich. plant was also analysed and the results are also given in Table 2 for information, although no further work was done with this ash.

TABLE 2. ANALYSIS OF ORIGINAL SAMPLES

Element	Sludge A	Sludge B gms/kg. dry solids	Cake B	Incinerator Ash
Ca	40.1	4.42	5.77	12.9
P	32.8	39.8	32.5	88.7
Fe	52.4	31.0	27.7	61.5
Cu	1.10	0.83	0.81	1.80
Pb	2.04	0.42	0.43	Nil
Ni	.082	1.28	1.28	2.38
Zn	3.33	5.9	5.9	8.0
Al	9.27	35.9	29.0	74.0
Cr	3.30	3.79	3.49	6.07
Mn	0.53	0.95	0.89	1.59
Mg	5.20	4.24	3.49	8.24

The results for metals and phosphate content are within normal ranges for most elements. Calcium is high in Sludge A, indicating some lime addition for pH control. The high iron in Sludge A and the high aluminum in Sludge B are the direct result of ferric chloride and alum additions, respectively, for phosphorus precipitation. High values of lead in Sludge A and of nickel in Sludge B and Cake B are indicators of specific industrial activities in the area served by the plants. For these amounts of lead and nickel, the level would be of concern if the sludge were used on agricultural land. The incinerator ash is correspondingly rich in nickel. Lead may or may not appear in incinerator ash depending on the incineration temperature since much of it is readily volatilized.

#### Extraction Tests - Anaerobic Sludge A and Filter Cake A

Three extraction tests were performed, two on digester underflow, each at different acid dosages, and one on the reslurried sludge filter cake. Experimental conditions are summarized in Table 3.



TABLE 3. EXTRACTION CONDITIONS

Test No.	Final pH	Grams Sample Used	mls. conc. H <sub>2</sub> SO <sub>4</sub> (97%)	Acid/Sludge Solids Weight Ratio
1	1.5	Digester Underflow 500 grams	4.3	0.483
2	0.8	Digester Underflow 500 grams	9.5	1.068
3	1.5	Sludge Filter Cake 400 grams	10.4	0.318

Extract solutions were analysed for important metallic elements. These results are shown in Table 4.

TABLE 4. ANALYSIS OF EXTRACT SOLUTIONS

Element	Extract 1		Extract 2		Extract 3	
	Amount Extracted gms/kg solids	%	Amount Extracted gms/kg solids	%	Amount Extracted gms/kg solids	%
P	32.9	100	32.0	97.5	25.6	78.0
Fe	51.6	98.6	54.2	100	50.8	96.9
Cu	0	0	.03	2.7	0	0
Al	6.81	73.5	7.43	80.2	5.45	58.9
Pb	0.66	32.3	0.68	33.3	0.19	9.3
Cr	2.53	76.6	3.23	97.9	1.83	55.5
Zn	2.97	89.2	3.23	97.0	2.33	70.0
Mn	0.54	100	0.55	100	0.54	100

From these results, the degree of extraction of metals and phosphates is generally linked, up to a point, with the amount of acid used per unit weight of sludge solids. Phosphate, aluminum, chromium and zinc all show improved extractions at higher acid usage levels. Iron and manganese are fully

extracted at all levels. All the iron is in the ferrous state, and hence all the copper is in the cuprous form, which explains the negligible extraction of copper. The lead forms the sparingly soluble sulfate, and the degree of extraction of this element therefore depends on the concentration of the  $PbSO_4$  in the solution. Since Extract 3 was much more concentrated than the other two (almost four times the sludge solids concentration) the reduced lead extraction for this case is probably only a reflection of the limited solubility of lead sulfate. The generally poorer extraction from the sludge filter cake is due primarily to the inadequate acid addition (only about two thirds of that required for good extraction). Because of the very small nickel content, it is not reported. Similarly, calcium is not reported because it forms the slightly soluble calcium sulfate.

Total dissolved solids, volatile solids and ash contents were determined for the extract solutions, with results as shown in Table 5.

TABLE 5. SOLIDS CONTENT OF FILTERED EXTRACTS

	Extract 1	Extract 2	Extract 3
Dissolved Solids			
kg/m <sup>3</sup>	11.67	24.13	27.13
kg/kg orig. sludge solids	.775	1.603	.467
Volatile Solids			
kg/m <sup>3</sup>	6.05	6.27	11.62
kg/kg orig. sludge solids	.402	.417	.200
Ash			
kg/kg dissolved solids	.309	.156	.381
kg/kg orig. sludge solids	.240	.250	.178

The dissolved solids from extract 2 contained a considerable amount of unreacted sulfuric acid, and hence this value was difficult to obtain accurately and is much higher than that for Extract 1. This suggests that the correct amount of acid needed for reasonably complete extraction of those elements readily soluble in sulfuric acid is just a little more than that used to prepare Extract 1, that is, of the order of 0.5 kg. of acid per kg. of sludge solids. The ash content based on original sludge solids is abnormally low for Extract 3 because of the incomplete extraction. As expected, the inorganic salt content (as reflected by ash) of the extract increases as more acid was used for the extraction, although the difference between Extract 1 and Extract 2 is small.

The washed residual solids from the extraction tests were also characterized with respect to fraction of the original sludge solids as insoluble residue, ash content of residual solids, calorific value of dry residual solids and moisture content of the cake as obtained from a standard filter leaf test. Results are shown in Table 6, together with the values for the original sludges.

TABLE 6. EXTRACTION RESIDUES

Sample	% Residual* Solids	% Ash in Residue	% Moisture in Sample or Filter Cake	Calorific Value joules/kg (kcal/kg) Dry Residual Solids	% Volatile Solids in Residue	% Ash Removed
Sludge Filter Cake	----	46.40	85.49	12.32 x 10 <sup>6</sup> (2942)	----	----
Digester Underflow	----	47.62	96.84	-----	----	----
Extract 1 Residue	59.5	30.50	60.62	15.88 x 10 <sup>6</sup> (3792)	67.7	61.9
Extract 2 Residue	51.1	27.40	61.88	17.40 x 10 <sup>6</sup> (4155)	70.3	70.6
Extract 3 Residue	76.8	39.04	65.6	14.48 x 10 <sup>6</sup> (3458)	59.5	37.0

\*Because of the addition of sulfate ion, the sum of dissolved solids in the extract plus residual solids is greater than 100% of original sludge solids.

All of the extraction residues have been substantially reduced in ash content by the extraction, more or less in proportion to the amount of acid used, up to a weight ratio of acid/sludge solids of about 0.6. A corresponding increase in calorific value occurs, with the best case, Extract Residue 2, showing an increase of 41.2%. The recommended acid usage as shown by Extract Residue 1 gives an increase of 28.9% in calorific value, and the incomplete extraction in Residue 3 shows an increase of 17.5%. The filter cakes formed, which were of much lower moisture content than the sludge filter cake presently used as incinerator feed, showed improved filtration rates, but did not wash well.

Total organic carbon analyses and COD analyses were carried out on the extracts and extract residues. Results are shown in Table 7.

TABLE 7. TOC AND COD ANALYSES

Sample	TOC gm/kg original sludge solids	COD
Extract 1	22.5	62.8
Extract 2	32.0	81.7
Extract 3	-----	79.5
Extract Residue 1	172.7	631.9
Extract Residue 2	138.4	600.4
Extract Residue 3	-----	731.8
Digester Underflow	214.3	729.9
Sludge Filter Cake	-----	812.5

The total organic carbon and COD both show somewhat less organic carbon reporting in the extract and residues than appeared to be present in the original sludge solids. It is possible that the values for TOC or COD are somewhat high for the original sludge because of the presence of carbonate and sulfide ions in this anaerobic product, and both of these species are destroyed by the acid extraction step. However, the most important feature of these results is the conclusion that the extraction with acid removes only about 10% of the total organic carbon or COD and the remaining 90% is in the residue. Since much of this "soluble" organic carbon is probably associated with the sludge liquid—all soluble solids in the sludge liquid become part of the extract - then it can be concluded that the extraction with sulfuric acid is quite highly specific for the inorganic constituents of the sludge.

#### Filterability of Sludges and Acidified Sludges

Original digester underflow and re-slurried sludge filter cakes were both tested with respect to filterability the same day as sampling was done, in order to minimize aging effects in storage. After acid extraction, in each of the three tests done, the extract solution was subjected also to filterability tests. Both Buchner funnel and filter leaf tests were done, as explained in Section 5. Filter leaf performance is expressed as  $\text{kg/m}^2 \text{ hr.}$  based on a 3 minute dewatering + washing cycle and 20 cycles/hour. The specific cake resistance as measured by the Buchner funnel test is given as  $\text{m/kg}$ , calculated from the formula

$$r = \frac{2 b P A^2}{c\mu}$$

where  $b$  - slope of a plot of  $\theta/V$  vs  $V$  where  $\theta$  is the time and  $V$  the filtrate volume,  $s/m^6$

$P$  - differential filtration pressure,  $N/m^2$

$A$  - filtering area,  $m^2$

$c$  - solids concentration in the slurry,  $kg/m^3$

$\mu$  - viscosity of the filtrate,  $N s/m^2$

Results of filtration tests are shown in Table 8.

TABLE 8. FILTRATION TESTS

Sample	Temp. °C	Filter Cake Resistance, r m/kg	Filter Leaf Yield kg/m <sup>2</sup> hr	Cake Moisture %
Digester Underflow	15	$6.62 \times 10^{13}$	0.859	
	30	$9.45 \times 10^{13}$	0.983	
Filter Cake (Re-slurried)	21	$1.29 \times 10^{13}$	0.497	
	21	$1.20 \times 10^{13}$	0.497	
Extraction 1 Slurry	65	$2.10 \times 10^{13}$	1.242	60.6
Extraction 2 Slurry	65	$2.10 \times 10^{13}$	0.695	61.9
Extraction 3 Slurry	65	$0.92 \times 10^{13}$	6.41	65.7

It is apparent from these results that there is only a rough correlation between the Buchner funnel results and the filter leaf results. The filter leaf results for extractions 1 and 2, in which digester underflow sludge was used, suggest only a little improvement in filterability following the acid extraction and heating. However, in every case when measured as filter cake resistance on the Buchner funnel, the acid treatment gave a somewhat improved filterability. This is in agreement with results published previously by Scott and Horlings (15), and found to be generally true for anaerobically digested chemical sludges, whether iron or alum has been added as a phosphorus precipitant (e.g., (21)(22)).

The more concentrated slurry used in extraction 3 (reslurried sludge filter cake with about four times the solids content of extractions 1 and 2) suggests a marked improvement in filterability might occur in these cases. However, the moisture contents of the cakes formed on the filter test leaf are much lower than that of the sludge filter cake from the plant sample.

The specific cake resistance values for the digester underflow without the addition of polymeric coagulants are well within the range quoted by Metcalf and Eddy (23) for anaerobically digested sludges.

#### Precipitation from Extract Solutions

According to the results reported by Scott and Horlings (15), when the iron exists in solution largely in the ferrous form, a partial separation between iron and heavy metals can be made by bringing the pH to the range of 4.0-5.0. The heavy metal precipitate (largely metal hydroxides and phosphates) can then be filtered off with the possibility of recovering and recycling soluble iron from the extract.

As recommended by Scott and Horlings, lime was added to each of the three extract solutions until the pH was 4.5. The precipitate was then filtered off and the filtrate analysed. Lime additions were 2.54 kg/m<sup>3</sup> of extract, 12.6 kg/m<sup>3</sup> and 5.4 kg/m<sup>3</sup> for Extracts 1, 2 and 3 respectively. Results are shown in Table 9.

TABLE 9. PRECIPITATION TEST AT pH 4.5

Element	Extract 1 % Removal	Extract 2 % Removal	Extract 3 % Removal
P	49	47.5	45.9
Fe	22.8	14.1	18
Zn	31.8	29.1	51.1
Cr	75.8	52.3	77.1
Al	94.9	97.5	96.4
Pb	100	100	100

It can be seen from the tabulated results that about half the phosphate was removed and much of the chromium, aluminum and lead, with the zinc having only a minority removed. These results are in agreement with those reported by Scott and Horlings (15). Filterability of precipitates was poor for Extracts 1 and 3, but good for Extract 2, presumably because of the additional calcium sulfate formation which acted as a filter aid. Results are reasonably comparable among the various extracts, although Extract 3 is nearly four times as concentrated as the other two. (Extracts used in this work contained from 1-5 kg/m<sup>3</sup> of metallic cations, and had been diluted by a factor of two from their maximum feasible strength).

The filtrate obtained from this treatment with lime in a plant in which extracts were not unreasonably diluted would contain about 1.2-1.5 kg/m<sup>3</sup> of ferrous iron, about 0.48 kg/m<sup>3</sup> of phosphorous, 0.064 kg/m<sup>3</sup> of zinc and small

amounts of other metals. The filtrate could be brought to a higher pH (approximately 7.0) which would then cause a precipitate to form consisting almost entirely of ferrous phosphate.

Some work was also carried out as part of a Masters program (21) on an anaerobically digested chemical sludge from a small treatment plant (Guelph, Ontario, Canada) to which alum had been added as a phosphate precipitant. An extract solution was made by the same procedure as used here (extraction at pH 1.5) and then this extract solution was subjected to fractional precipitation by the addition of sodium hydroxide. Figures 1 and 2 show the change in extract composition as a function of pH and the percentage precipitation of the various elements. In this solution, larger than usual amounts of magnesium and aluminum occurred (9.8 gms/kg of dry sludge solids for Mg and 34.1 gms/kg of dry sludge solids for Al). The behaviour of the phosphate, aluminum and magnesium shown is very interesting, and suggests that magnesium and aluminum ions can be used as specific agents for the removal of phosphates in the presence of other metals, particularly ferrous iron, by adjusting the pH to no higher than 3.0 with adequate amounts of Mg and Al present.

Extraction Tests - Waste Activated Sludge B and Mixed Sludge Filter Cake B

Five extraction tests were performed, three on the waste activated flotation sludge and two on the reslurried filter cake from the mixed aerobic and primary sludge. Experimental conditions are summarized in Table 10.

TABLE 10. EXTRACTION CONDITIONS

Test No.	Final pH	Grams sample used	mls conc. H <sub>2</sub> SO <sub>4</sub> (97%)	Remarks	kg. acid/kg. dry sludge solids
1B	1.5	flotation sludge 500 gms	4	no wash-water	.360
2A	0.8	flotation sludge 500 gms	15	no wash-water	1.348
3A	0.8	sludge filter cake 200 gms	12	no wash-water	.797
5	1.5	flotation sludge 500 gms	4	wash water added	.360
6	1.5	sludge filter cake 150 gms	4	wash water added	.365

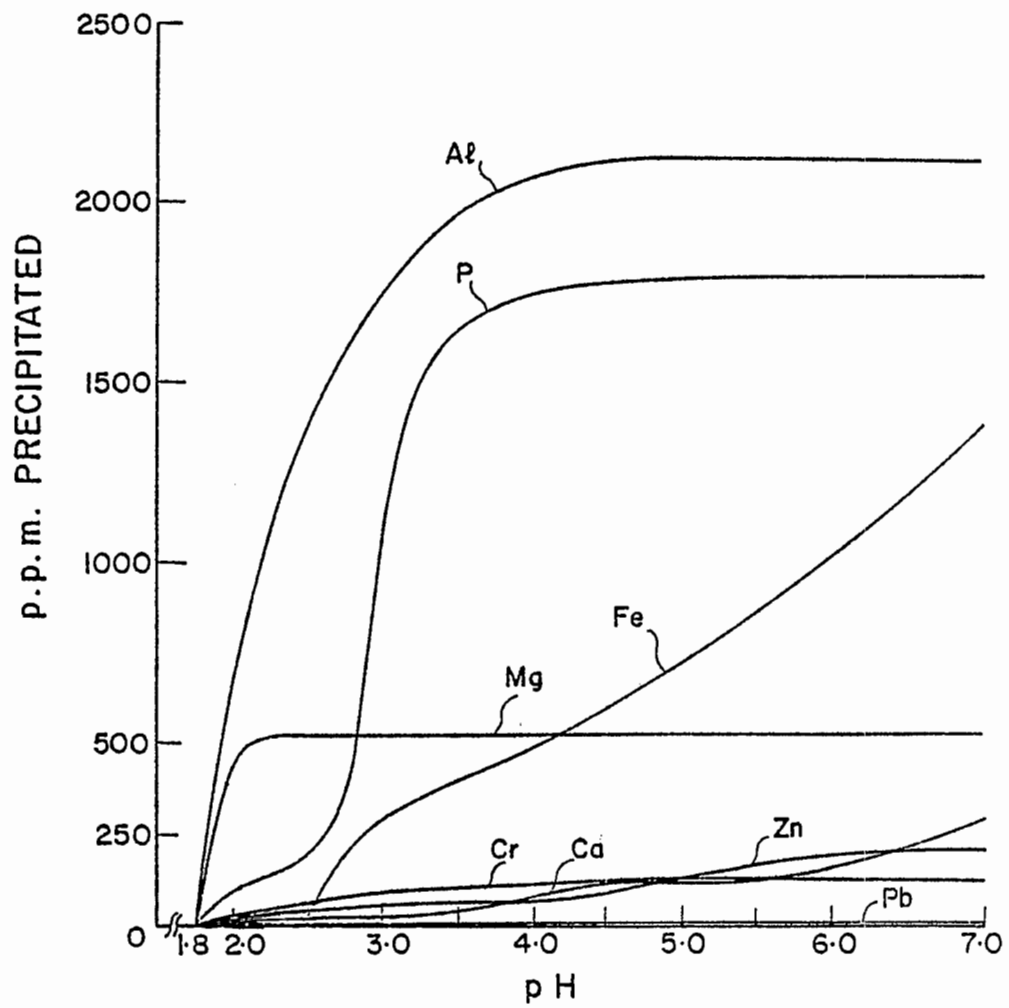


Figure 1. Amount of metals precipitated vs pH.



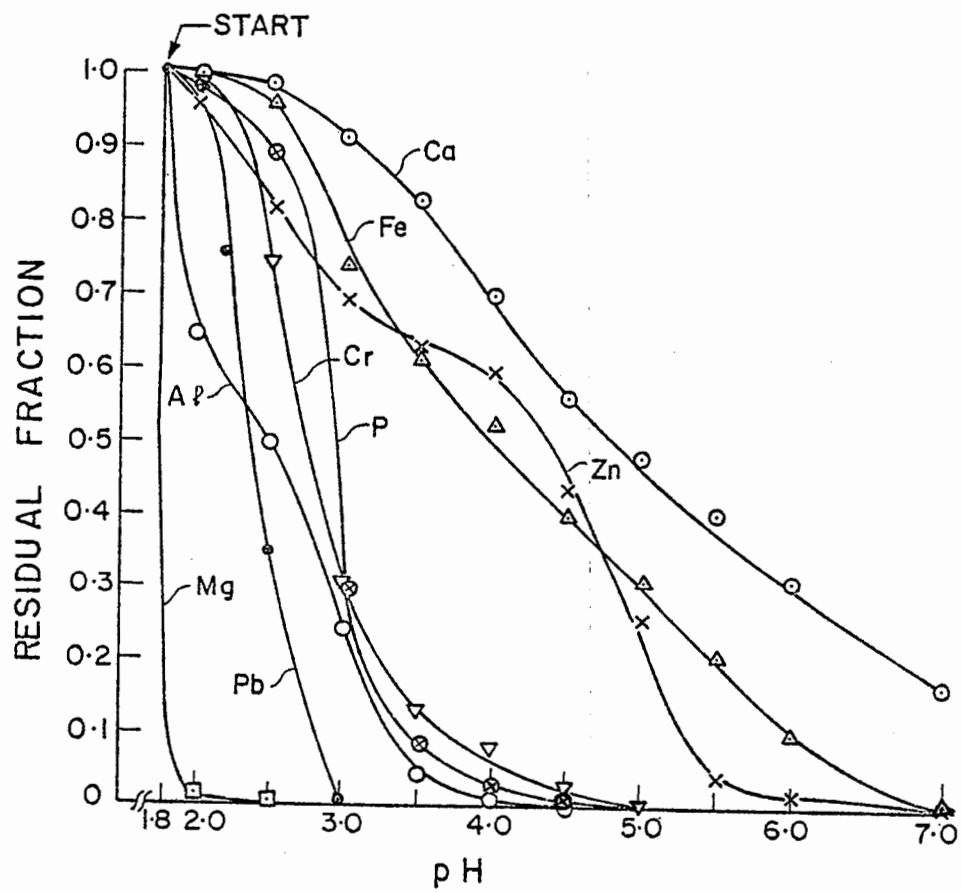


Figure 2. Residual fraction of metals in the extract as a function of pH.

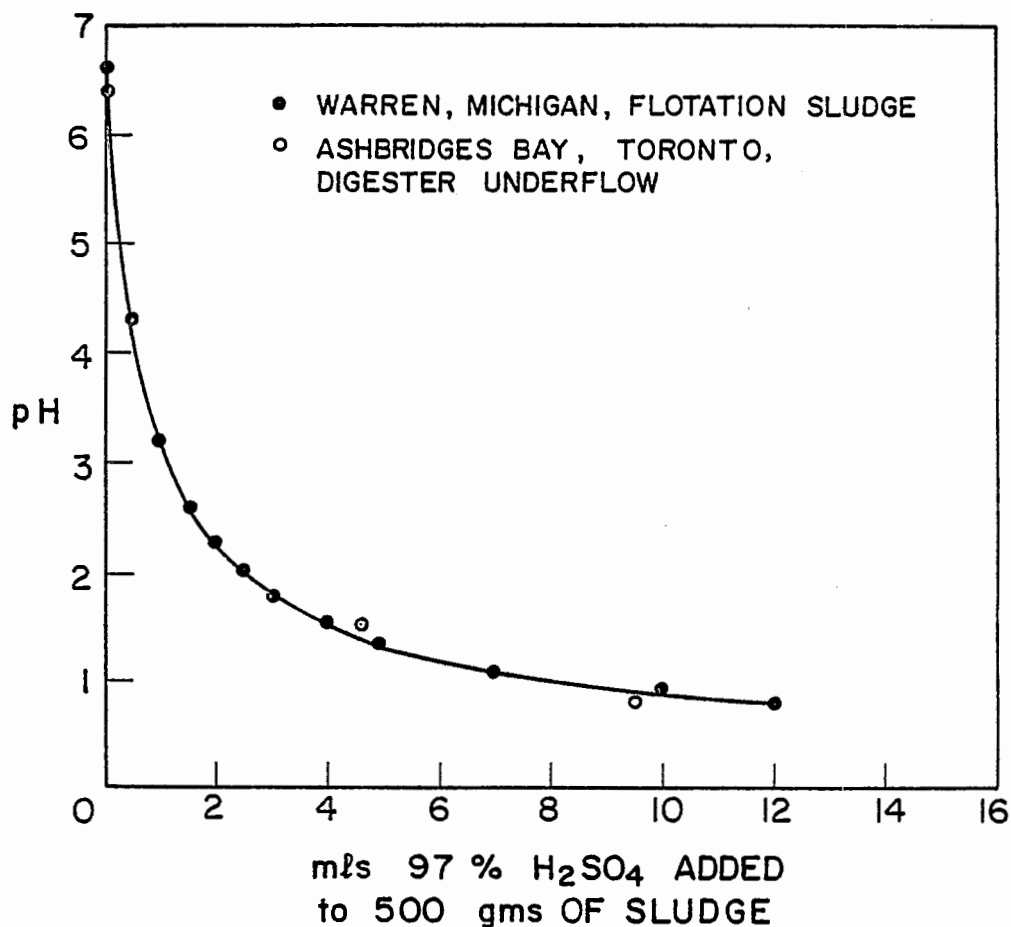


Figure 3. Acid requirement of sludge to attain a given pH value.

The variation of the final pH of the extract slurry of sludge and acid is shown in Figure 3, and the amount of acid used was selected from this chart to give the desired final pH. The curve also describes well the acid requirement of the anaerobic digester underflow from the Toronto plant, although the Warren flotation waste activated sludge was about 4.0% solids and the Toronto anaerobic sludge was only 3.2% solids, but the latter had a significantly higher metals content (25% more). In fact, the acid usage can be made comparable among different sludges by proportioning it to the sum of the iron, aluminum, calcium, magnesium and zinc contents, per unit of dry sludge solids, these elements accounting for the great majority of cationic equivalents in the sludge which consume acid. Hence, the two sludges shown in Figure 3 fall on the same line because they happen, fortuitously, to contain the same amount of these cations per unit volume of total sludge. Figure 3 also shows the buffering effect of the sludge solids at lower pH values. This effect makes

it difficult to precisely predict acid requirements for lower pH, and is mainly responsible for the different amounts of acid per unit of solids apparently needed to achieve a pH of 0.8 for the flotation sludge and the mixed sludge filter cake.

In Table 10 the comment "no wash-water" means that the extract was analyzed and the percent solubilization of a species calculated based on the known total liquid volume. The phrase "wash-water added" means that the extracted residue was washed, and the percent extraction based on the amount of the particular species found in the filtrate plus washings. Since the residual solids washed poorly, this method gives a lower extraction yield. Extraction yields for the five tests are given in Table 11, and the lower extraction yields shown in tests 5 and 6 compared to test 1B, for example, are indicative of the difficulty in washing residual solids. Apparently, up to 25% of the solubilized material may be retained in the residual solids unless they are adequately washed.

TABLE 11. PERCENT EXTRACTION OF METALLIC ELEMENTS

Element	Extract No.				
	1B	2A	3A	5	6
P	78	92	83.0	66.5	70.5
Fe	81	98	99.6	72.6	74.7
Al	96.8	100	93.9	76.0	74.1
Zn	100	100	97.9	67.5	64.2
Mg	100	100	96.3	78.5	78.8
Ca	39	74	66	20.8	25.6
Ni	100	100	100	78.1	75.8
Cu	94.5	100	73.1	7.7	0.7
Cr	100	98.8	91.9	60.9	66.7
Mn	100	100	100	100	90.9
Pb	0	0	0	0	0

The above results indicate that adequate extraction, about 80%, of iron and phosphorus can be achieved at an acid usage of 0.4 kg/kg. original sludge solids, that is, at a final pH of 1.5 in the extract. At this level of acid usage, essentially complete extraction of all minor metals having soluble sulfates is achieved. This is an important result, for it shows that a

minimum acid usage will completely solubilize injurious heavy metals, with the exception of lead, in both the waste activated sludge and the mixed sludge. For this sludge, in particular, it is encouraging to note the high level of extraction of zinc, nickel and chromium. Copper appears to be soluble in acidic solution but re-precipitates at higher pH, that is, during washing with neutral water (compare tests 1B and 5).

In addition to the degree of extraction, the total dissolved solids, the fraction of volatile solids and the ash content of the dissolved solids from the washed residue solids (tests 5 and 6) were determined and are given in Table 12.

TABLE 12. SOLIDS CONTENT OF FILTERED EXTRACTS

	Extract 5	Extract 6
Dissolved Solids		
kg/kg orig. sludge solids	0.560	0.519
Volatile Solids		
kg/kg orig. sludge solids	0.24	0.261
kg/kg extract solids	0.429	0.503
Ash		
kg/kg orig. sludge solids	0.251	0.196
kg/kg extract solids	0.448	0.378

The washed residual solids from extraction tests 5 and 6 were also characterized with respect to total dry solids, volatile solids fraction and ash content and these values are given in Table 13. Calorific values are also given in Table 13, expressed per unit weight of dry solids for the solid specified.

TABLE 13. EXTRACTION RESIDUES

Sample	% residual solids	% volatile solids in residual solids	% ash in residual solids	Calorific value (kcal/kg) dry residual solids	% ash removal
Flotation sludge	--	57.24	34.89	18.03 x 10 <sup>6</sup> (4306)	
De-watered filter cake	--	61.28	32.5	21.08 x 10 <sup>6</sup> (5033)	
Extract 5 Residue	73.1	62.20	21.00	23.51 x 10 <sup>6</sup> (5614)	56.0
Extract 6 Residue	70.2	73.79	23.15	22.26 x 10 <sup>6</sup> (5315)	50.0

COD analyses were carried out on extracts and original sludge samples. Results are shown below in Table 14.

TABLE 14. COD ANALYSIS

Sample	COD (gms/kg dry orig. sludge solids)
Extract 5	157
Extract 6	138
Flotation sludge	970
De-watered filter cake	1157

The larger COD value of the de-watered sludge compared to that of the flotation sludge can partly be accounted for by the COD of the polymeric flocculant added prior to filtration.

A solids material balance based on results in Tables V and VI cannot really be carried out because of the loss of some volatile material, for example, carbon dioxide, on acidification. In general, however, the sum of (original sludge solids + sulfate added) is only 2% - 5% higher than the sum of (dissolved extracted solids + residual solids).

Results in Tables 11, 12 and 13 show clearly the selective nature of the extraction, that is, organics remain largely with the residue while the

extract solids have a high proportion of inorganic material. The higher volatile solids content and calorific value of the filter cake is due to the content of primary sludge in this material. The smaller increase in calorific value of the filter cake after extraction appears to be due to the less effective extraction of inorganics in Test #6. The degree of extraction of inorganics could be significantly improved with a resulting decrease in ash and increase in calorific value with adequate washing of the residual solids.

Even with the poor washing in these tests, the results show that the residual solids would yield only 44% (for the waste flotation sludge) to 50% (for the filter cake) of the ash weight after incineration that would result from the present sludge feed. Calorific values of the sludge solids would increase from 30% (flotation sludge) to 6% (filter cake). The COD appears to remain to a very large degree in the residual solids.

Hence, the beneficial results of acid extraction are of the same degree for these aerobic and mixed sludges treated with alum as was found for thickened anaerobic sludge treated with ferric chloride.

#### Filtration Behaviour

Filtration tests using the Buchner funnel technique were carried out on the waste activated sludge and on re-slurried filter cake. In the plant, polymeric additives are used to attain adequate filtering or settling rates. The beneficial effects of polymer additives are transitory, and hence by the time samples were tested in the laboratory, aging had occurred to the point where filtration results were not comparable to operating plant values. Hence, laboratory numbers have no absolute significance. Filtration tests did show clearly, however, that for the aerobic waste activated sludge, or for the mixed sludge, acid treatment had no significant effect on filterability, neither increasing nor decreasing filtration rates. Tests on fresh plant samples would be necessary to determine if the lowered pH after acid treatment significantly affected the effectiveness of polymeric flocculants. Because it would be preferable in plant practice, although probably not essential, to have reasonably good washing of extract residues after acid treatment, this aspect of filterability and washing effectiveness would need to be further investigated.

Filter cake resistance,  $r$ , as measured by the Buchner funnel test was  $3.46 \times 10^{13}$  m/kg, well within the usual range of values for aerobic or mixed sludges as given by Metcalf and Eddy (23).

#### Ash Fusion Points

Harkness et al (24) present data for both the softening point and the fusion point of ash from incinerated digested sludges, some of which contained iron as a phosphate precipitant, and some aluminum (added as aluminum chloride hydrate). Wide variations in iron content were found to cause essentially no change in fusion temperature and little in softening point. Similarly, aluminum content up to 26% in the ash tended to raise the softening point and the fusion point very slightly in oxidizing conditions. In reducing conditions,

high aluminum content appeared to decrease the softening and fusion points noticeably.

Some tests were carried out in earlier work (21) on an anaerobically digested sludge which contained a fairly high iron content (Iron had been used as a phosphate precipitant). Aluminum content was low. Ash softening points and fusion points were measured in a mildly reducing atmosphere for the ash produced by the residual acid-extracted solids as well as for the ash from the unextracted sludge. In addition, an unextracted filter cake which had been heavily conditioned with lime and ferric chloride prior to de-watering was ashed, and softening and fusion points determined. Results are given below.

TABLE 15. ASH FUSION POINTS

Sample	Softening Point °C	Fusion Point °C
Extracted Residual Solids	1170	1200
Unextracted Sludge Solids	1240	1280
Conditioned Filter Cake	1160	1210

Experience of others suggests that limited amounts of some metals in the ash may be beneficial in raising the softening point, but excessive lime or iron can be detrimental, that is, they can reverse the gain obtained by small contents. However, the results in Table 15 indicate, in agreement with the results of Harkness et al, that wide ranges of variation in iron or aluminum contents in the ash do not lead to any but minor changes in softening or fusion points.

## SECTION 7

### ESTIMATES OF COST

#### Basis of Cost Estimate

Two preliminary cost estimates were carried out, one for each of the types of sludge studied in this work. The iron-rich anaerobic sludge was assumed to be available as the filter cake, and the amount was taken to be equal to that produced by the Ashbridge's Bay plant of the city of Toronto (180 mgpd input). Hence, this case represents a large scale of operations. The second estimate was made for the filter cake produced from the mixed sludge at the Warren, Michigan, plant (30 mgpd). Hence, this second case represents a medium size plant producing waste activated plus primary sludge without anaerobic digestion and rich in aluminum.

Filter cake was selected as a starting material since it is readily available, and the more concentrated solutions possible when starting with filter cake minimizes the process plant size for acid extraction. In both plants, only polymeric flocculants were added to the sludge to aid in dewatering, and hence sludges and filter cakes have essentially the same compositions.

The process envisaged consists of the units listed below for each case, together with important operating parameters. All process units are of plastic or lined steel construction.

#### Large Plant

180 mgpd (Imperial), iron rich anaerobically digested sludge.

Basis - 1200 lbs. of sludge for  $10^7$  lbs. of influent  
Filter Cake slurried to 10% solids  
Acids usage 0.48 kgs/kg. dry sludge solids  
Plant operates 330 days per year, 24 hours per day

Sludge solids produced - 32400 tonnes/year  
98181 kg/day

Acid (100% H<sub>2</sub>SO<sub>4</sub>) - 15550 tonnes/year  
48576 kg/day



1. Extraction Tank - residence time 20 minutes, 20°C  
Volume 4000 U.S. gals.
2. Hot Tank - residence time 5 minutes, 95°C  
Volume 1000 U.S. gals.
3. Heat Exchangers, one exchanging effluent from hot tank with  
influent 68 m<sup>2</sup> area, second steam heated with low pressure  
steam 23 m<sup>2</sup> area.
4. Filter for extract slurry, rotary vacuum, 65°C  
58420 kgs. solids/day = 2434 kgs solids/hr.  
Area 200 m<sup>2</sup>  
Wash water 29000 kgs/hr.  
Cake to incineration  
Extract to precipitation tank
5. Precipitation tank and 3 agitator 3000 gals.  
Lime added 5 kg/m<sup>3</sup> (pH 4.0)  
Mg<sup>++</sup> added
6. Rotary vacuum filter, 20 m<sup>2</sup>  
Cake to phosphate recovery  
Filtrate to phosphate removal section of treatment plant

Metals in Extract Solution before Precipitation (estimated from Table 4)

	<u>kg/day</u>	<u>tonnes/yr.</u>
P	3063	1011
Fe	4880	1610
Al	638	211
Mg	511	168
Zn	275	91
Cr	236	78
Pb	65	21

Metals in recycle to treatment plant\*

	<u>kg/day</u>	<u>tonnes/yr.</u>
Fe	4291	1416
Zn	206	68
Cr	118	39
P	153	51
Al	32	11

\* Fractional precipitation estimated from Table 9, and Figure 5 of reference (15).

Total fixed capital investment required with process equipment costs from Woods (25) adjusted to 1979 and using Lang factors for a solids-fluid plant is \$1,220,000.

Annual cost of production with  $H_2SO_4$  at \$50/tonne,  $Ca(OH)_2$  at \$40/tonne, 10% depreciation per year = \$2,460,000/yr = \$41.41 per million gallons.

Credit for Fe produced = \$350/tonne of Fe = \$496,000/yr = \$8.35/million gallons. No operating costs have been included.

Net cost of treatment is \$33.06 per million gallons.

Depending on the treatment of the precipitate cake, the credit for the phosphate produced will just about pay for the cost of further processing. Hence, the value of the phosphate and metals in the cake (Al, Mg, Pb, Zn,  $Fe^{++}$ , Cr) is just about enough to allow further refining so they can be marketed.

The above conclusion is based on a scheme whereby the cake is extracted with ammonia to solubilize Zn, Cr, Ni, Cu. The extract is boiled to recover ammonia and the metal hydroxides and oxides precipitated, recovered, and sold. The residue containing P, Mg, Al, Pb,  $Fe^{+++}$  is treated with sodium hydroxide solution to a pH of 12 which removes the Al and Pb. The resulting solid, which is mainly magnesium or ferric phosphate, can then be marketed.

No credit has been taken for the decreased incinerator ash volume which must be handled, or the increased calorific value of the sludge.

Medium Plant

30 mgpd (U.S.), aluminum rich mixed sludge filter cake.

Basis - 1500 lbs. of sludge per million U.S. gallons of influent  
 Filter cake slurried to 10% solids  
 Acid usage 0.36 kg/kg. dry sludge solids  
 Plant operates 330 days/year; 24 hours/day

Process is identical to that proposed for the large plant, except filtrate from precipitation tank goes to waste.

Estimated metals in extract solution before precipitation, assuming average washing (from Table 1).

	<u>Assumed % extraction</u>	<u>kg/day</u>	<u>tonnes/yr.</u>
P	75	497	164
Fe	78	442	146
Al	85	503	166
Zn	80	97	32
Mg	90	64.2	21.2
Ni	80	20.9	6.9
Cu	10	1.5	0.5
Cr	80	57.0	18.8
Mn	95	17.3	5.7
Pb	0	0	0

Assuming precipitation at pH 4.0, based on Figure 2, metals and phosphates in cake allowing for the fact that iron is in ferric form,

	<u>kg/day</u>	<u>tonnes/yr.</u>
P	473	156
Fe	442	146
Al	503	166
Zn	48.5	16
Mg	64.2	21.2
Ni	20.9	6.9
Cr	57.0	18.8

To recover aluminum salts for recycle in the waste water treatment plant the precipitated cake is treated with ammonia to solubilize and remove Zn, Ni and Cr. These are then precipitated by boiling and can be sold as a mixed metal oxide. The residual cake is then treated with sodium hydroxide solution at pH 12 to solubilize the aluminum. The residue, containing Fe, Mg and phosphate primarily, can be sold for its phosphate content.

Fixed Capital investment cost (using six-tenths rule) = \$420,000

Cost of operations, including depreciation at 10% per year = \$824,210 per year.

Credit for recycle of aluminum salt \$160,000/year

Credit for phosphate and metals \$162,000/year

Net cost of process = \$50.70 per million gallons of influent.

### Discussion

The capital costs for this process are quite reasonable, and fixed costs are only a small part of the annual total costs. The major cost is for chemical reagents - 64% of the total cost of production for the large plant and 58% for the medium plant. Hence, less expensive techniques to separate iron or aluminum and phosphate from the extract liquor would be most effective in reducing costs. Solvent extraction has been suggested as one possibility.

In carrying out the cost estimates, it was assumed that adequate washing of residual extracted solids was possible with reasonable amounts of wash water. This can be achieved with anaerobic sludges, but the mixed aerobic-primary sludge would need some conditioning prior to de-watering, for adequate washing.

In general, costs for an acid extraction process might be within reason for large plants if the benefits gained in the incineration process and the reduced cost of ash disposal were deemed to be of comparable value. For medium size plants, the process is unlikely to be economical unless some inexpensive way of processing the extract solution is developed.

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16. ABSTRACT The purpose of this work was to look at the technical and economical aspects of acid extracting heavy metals and phosphates from municipal chemical sludges and subsequently recovering them by lime neutralization. The results showed that such a process was technically feasible, but the cost of the process was economically unattractive. The results should be valuable in assessing similar technology for removing heavy metals from municipal sludges.		
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